Crossover Corresponding State Model for Pure Fluids and Nuclear Matter

S.B Kiselev,[1,C,S] J.F. Ely,[1] and I.V. Kononenko[2]

[1]*Chemical Engineering Department, Colorado School of Mines*
1500 Illinois St., Golden, CO 80401-1887, U.S.A.

[2]*Gubkin Russian State University of Oil and Gas, Moscow, Russia*

A cubic equation of state (EOS) is the simplest equation which predicts the existence of the critical point and allows an explicit formulation of corresponding states (CS). Unfortunately, however, a cubic EOS gives only qualitative representation of the vapor-liquid equilibrium (VLE) in real fluids, and the quantitative difference between theory and experiment is rather substantial, especially in the critical region. In order to improve the critical-region representation given by a cubic EOS, one needs to superimpose the effects of long-scale density fluctuations. In this study we incorporate the non-analytic scaling laws that arise from long-scale density fluctuations into the classical cubic EOS using a general crossover procedure proposed by Kiselev [1]. Using the Patel-Teja (PT) EOS [2] as a reference EOS, we first developed a new crossover cubic (CRC) EOS for one-component fluids. The new CRC EOS was tested against an extensive set of experimental data for the volumetric and caloric properties of different pure fluids. The CRC EOS contains 10 adjustable parameters and reproduces the pressures at $T7T_c$ with an average absolute deviation (AAD) less then 1%, and the liquid densities at $\rho 72\rho_c$ with AAD of about 1-2%. In the temperature region $T>T_c$, the CRC EOS reproduces the saturated pressure data with AAD of about 0.5-1%, the liquid density data with AAD of about 1%, and the vapor density with about 2-3%. Unlike the previous crossover cubic EOS [1,3], the new CRC EOS based on the parametric sine model and can be analytically extended into the metastable and unstable regions and reproduces the asymptotic scaling behavior of the isochoric heat capacity in the one- and two-phase regions.

In the second part of this study we have made the new CRC EOS more predictive by applying the corresponding states principle. In addition to the critical compressibility Z_c and acentric factor ω used in classical CS models, the CR CS model also requires the Ginzburg number, *Gi*, as input. For pure fluids we found a simple empirical relationship $Gi(\omega, Z_c)$ and applied this model for the prediction of the PVT and VLE properties of more than 30 pure fluids in a wide range of thermodynamic conditions, including the nearest vicinity of the critical point. The CR CS model reproduces the PVT-surface of one-component fluids (polar and non-polar) with practically the same accuracy as the CRC EOS. We also show that in a more general formulation, with *Gi* as a free parameter, the CR CS model is also capable of describing the liquid vapor coexistence of finite neutral nuclear matter experimentally observed recently in ^{197}Au [4,5].

[1] S.B. Kiselev, Fluid. Phase. Equilib., **147**, 7 (1998).
[2] N.C. Patel and A. S. Teja, Chem. Eng. Sci., **37**, 463 (1982).
[3] S.B. Kiselev and D. G. Friend, Fluid. Phase. Equilib., **162**, 51 (1999).
[4] M.K. Berkenbusch, W. Bauer, K. Dilliman, *et al*., Phys. Rev. Lett., **88**, 042701 (2002).
[5] J.B. Elliott, L.G. Moretto, L. Phair, *et al*., Phys. Rev. Lett., **88**, 022701 (2002).